L. Dean A. Hauck

Argonne National Laboratory

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 7. The Corrosion of Nickel
in Process Environments

by

A. A. Chilenskas and G. E. Gunderson

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

*Part 7. The Corrosion of Nickel
in Process Environments*

by

A. A. Chilenskas and G. E. Gunderson

Chemical Engineering Division

March 1965

Other reports in this series are:

Part 1: Bench-scale Investigation of a Process for Zirconium-Uranium Alloy Fuel, by D. Ramaswami, N. M. Levitz, J. T. Holmes, and A. A. Jonke (ANL-6829).

Part 2: Bench-scale Investigation of a Process for Aluminum-Uranium Alloy and Stainless Steel-Cermet Fuels, by D. Ramaswami, N. M. Levitz, and A. A. Jonke (ANL-6830).

Part 3: Fluid-bed Fluorination of Uranium Dioxide Fuel Pellets, by L. J. Anastasia, J. D. Gabor, and W. J. Mecham (ANL-6898).

Part 4: Fluidized-packed Beds: Studies of Heat Transfer, Solids-Gas Mixing, and Elutriation, by J. D. Gabor and W. J. Mecham (ANL-6859).

Part 5: Description of a Pilot-scale Facility for Uranium Dioxide-Plutonium Dioxide Fuel Processing Studies, by G. J. Vogel, E. L. Carls, and W. J. Mecham (ANL-6901).

Part 6: Preparation of Dense Uranium Dioxide Particles from Uranium Hexafluoride in a Fluidized Bed, by I. E. Knudsen, N. M. Levitz, and A. A. Jonke (ANL-6902).

Part 8: Pilot Plant Development of a Process for Uranium Alloy Fuels, by J. T. Holmes, H. L. Stethers, and J. J. Barghusen (ANL-6973).

Part 9: Computer Programs for Alloy-fuel Process Calculations, by J. T. Holmes and D. Ramaswami (ANL-6992).

Part 10: Bench-scale Studies on Irradiated Highly-enriched Uranium Alloy Fuels, by A. A. Chilenskas and K. S. Turner (ANL-6994).

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF FIGURES

LIST OF TABLES

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 7. The Corrosion of Nickel
in Process Environments

by

A. A. Chilenskas and G. E. Gunderson

ABSTRACT

Corrosion studies in support of the Fluoride Volatility Program are in progress. Two types of tests have been used for this program: small-scale laboratory tests conducted in tube furnaces, and in-plant exposure tests. The laboratory tests were designed to examine the effect upon nickel of short-term and long-term exposures of selected gaseous environments that were representative of gaseous environments found in Fluoride Volatility processing. The in-plant tests consist of exposing specimens within various pieces of pilot-plant equipment and evaluating the corrosion rates after the completion of one or more process cycles. The results of both types of tests show:

    1.   Under conditions of low gas flow rates, where protective films can easily form, the corrosion rate of nickel by fluorine alternated with hydrogen chloride and fluorine alternated with oxygen is low (1-4 mils/yr) and is in close agreement with the rate exhibited by nickel for fluorine alone.

    2.   Under conditions where films form less readily (high gas velocities) or can be removed upon being formed (fluid-bed impingement), the corrosion rate is significantly higher than that under static conditions but less than the rate that would occur if no protective film formed at all. Experimental evidence of the effect of a fluidized bed upon the corrosion rate of nickel shows that the rate is increased due to the presence of the bed. For the conditions studied, the corrosion rates in plant equipment would be expected to range between 12 and 40 mils/yr, the lower values existing in most of the components while the higher values would be expected for those components in contact with the fluid bed.

    3.   The corrosion rates obtained under "static" conditions for long-term exposure of two types of nickel welds have been compared. Nickel welds made with nickel-200 metal filler have been shown to be clearly superior to welds made with nickel-61 filler metal. The corrosion rates of welds made with nickel-200 range from 1-5 mils/yr (comparing

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 7. The Corrosion of Nickel
In Process Environments

by

A. A. Chilenskas and G. E. Gunderson

ABSTRACT

Corrosion studies in support of the Fluoride Volatility Program are in progress. Two types of tests have been used for this program: small-scale laboratory tests conducted in tube furnaces, and in-plant exposure tests. The laboratory tests were designed to examine the effect upon nickel of short-term and long-term exposures of selected gaseous environments that were representative of gaseous environments found in Fluoride Volatility processing. The in-plant tests consist of exposing specimens within various pieces of pilot-plant equipment and evaluating the corrosion rates after the completion of one or more process cycles. The results of both types of tests show:

1. Under conditions of low gas flow rates, where protective films can easily form, the corrosion rate of nickel by fluorine alternated with hydrogen chloride and fluorine alternated with oxygen is low (1-4 mils/yr) and is in close agreement with the rate exhibited by nickel for fluorine alone.

2. Under conditions where films form less readily (high gas velocities) or can be removed upon being formed (fluid-bed impingement), the corrosion rate is significantly higher than that under static conditions but less than the rate that would occur if no protective film formed at all. Experimental evidence of the effect of a fluidized bed upon the corrosion rate of nickel shows that the rate is increased due to the presence of the bed. For the conditions studied, the corrosion rates in plant equipment would be expected to range between 12 and 40 mils/yr, the lower values existing in most of the components while the higher values would be expected for those components in contact with the fluid bed.

3. The corrosion rates obtained under "static" conditions for long-term exposure of two types of nickel welds have been compared. Nickel welds made with nickel-200 metal filler have been shown to be clearly superior to welds made with nickel-61 filler metal. The corrosion rates of welds made with nickel-200 range from 1-5 mils/yr (comparing

closely with the corrosion rate for nickel plate, 1-4 mils/yr), while the welds made with nickel-61 filler metal ranged from 67-1315 mils/yr. Some evidence obtained indicates that the presence of a small amount of titanium in the nickel filler metal-61 is the cause of the high corrosion rates exhibited.

    4.   Specimens examined metallographically in both laboratory-scale and in-plant environments have exhibited little or no evidence of intergranular attack. Several specimens from the in-plant tests have shown a few areas where apparent intergranular attack ranging in depth from 1 to 2 mils has occurred.

    5.   Several parameters that were thought to have a possible effect upon the integrity of the protective film were studied for their effect upon the corrosion rate of nickel. Thermal cycling of a specimen exposed to process environments had little or no effect upon the corrosion rate. Exposure of the specimen to air after each process cycle also did not greatly affect the corrosion rate.

I. INTRODUCTION

    Fluid-bed fluorine volatility processes are being developed for the recovery of both uranium and plutonium from spent nuclear fuels. Nickel has been used extensively as a material of construction in both laboratory-scale and pilot-plant-scale equipment used in these studies. A corrosion program has been carried out over the past several years at ANL to examine the suitability of nickel as a material of construction for plant use. The types of tests employed were: (1) laboratory tests in which nickel specimens were exposed within furnace tubes to selected gases under closely controlled conditions of flow and temperature, and (2) in-plant tests in which nickel specimens were located in various places within pilot-plant equipment and exposed to processing environments. The results of these tests are presented and compared with each other, as well as with kinetic rate data.

II. THE LONG-TERM CORROSION OF WELDED AND NONWELDED NICKEL-200 PLATE IN "STATIC" GAS ENVIRONMENTS

A. Materials, Apparatus, and Experimental Procedure

    These tests were conducted by exposing nickel specimens, held in a nickel furnace tube, to various gas mixtures under conditions of gas flow such that the corrosion films that formed were not disturbed during the experiment. For the purpose of this report, this condition is designated as "static" gas flow. The nickel furnace tubes were heated with resistance furnaces, and the temperatures were measured by chromel-alumel thermocouples.

closely with the corrosion rate for nickel plate, 1-4 mils/yr), while the welds made with nickel-61 filler metal ranged from 67-1515 mils/yr Some evidence obtained indicates that the presence of a small amount of titanium in the nickel filler metal-61 is the cause of the high corrosion rates exhibited.

4. Specimens examined metallographically in both laboratory-scale and in-plant environments have exhibited little or no evidence of intergranular attack. Several specimens from the in-plant tests have shown a few areas where apparent intergranular attack ranging in depth from 1 to 2 mils has occurred.

5. Several parameters that were thought to have a possible effect upon the integrity of the protective film were studied for their effect upon the corrosion rate of nickel. Thermal cycling of a specimen exposed to process environments had little or no effect upon the corrosion rate. Exposure of the specimen to air after each process cycle also did not greatly affect the corrosion rate.

I. INTRODUCTION

Fluid-bed fluorine volatility processes are being developed for the recovery of both uranium and plutonium from spent nuclear fuels. Nickel has been used extensively as a material of construction in both laboratory-scale and pilot-plant-scale equipment used in these studies. A corrosion program has been carried out over the past several years at ANL to examine the suitability of nickel as a material of construction for plant use. The types of tests employed were: (1) laboratory tests in which nickel specimens were exposed within furnace tubes to selected gases under closely controlled conditions of flow and temperature, and (2) in-plant tests in which nickel specimens were located in various places within pilot-plant equipment and exposed to processing environments. The results of these tests are presented and compared with each other, as well as with kinetic rate data.

II. THE LONG-TERM CORROSION OF WELDED AND NONWELDED NICKEL-280 PLATE IN "STATIC" GAS ENVIRONMENTS

A. Materials, Apparatus, and Experimental Procedure

These tests were conducted by exposing nickel specimens, held in a nickel furnace tube, to various gas mixtures under conditions of gas flow such that the corrosion films that formed were not disturbed during the experiment. For the purpose of this report, this condition is designated as "static" gas flow. The nickel furnace tubes were heated with resistance furnaces, and the temperatures were measured by chromel-alumel thermocouples.

The fluorine used in these studies was purchased from the Allied Chemical Company and was passed through a heated sodium fluoride trap for the removal of hydrogen fluoride. The hydrogen chloride was purchased from the Matheson Company and used directly from the tank.

The gas environments studied were: (1) 50 v/o fluorine in nitrogen, (2) 50 v/o fluorine in nitrogen, alternated with 50 v/o hydrogen chloride in nitrogen, and (3) 50 v/o fluorine in nitrogen, alternated with 50 v/o oxygen in nitrogen. The gas mixtures were produced by metering the individual gas streams with rotometers and permitting them to mix in the inlet line before entering the furnace tube.

Nickel-plate samples, 3/4 by $2\frac{3}{16}$ in., were cut from 1/16- and 1/4-in. plate. The welded specimens were made from 3/16-in. plate. The specimens were made by welding two pieces of plate, 1/2 in. by $2\frac{3}{16}$ in. long, using full-penetration TIG welding* with nickel filler metal-61 or nickel filler metal-200.** The ends of the specimens were cut, and the four edges were ground with metallographic polishing paper to remove disturbed metal. The specimens were then stamped with an identifying number, degreased, and weighed. After exposure, the specimens were defilmed in an equimolar salt bath of potassium nitrate-sodium nitrate at 500°C for one-half hour. The specimens were reweighed, and the corrosion rate was calculated from the weight loss based upon the exposure time and original specimen area. Both the plate and welded specimens were sectioned, mounted in bakelite, and polished to a half-micron finish. These samples were etched, using freshly prepared and mixed solutions of 10% sodium cyanide and 10% ammonium persulfate. The samples were then examined microscopically for intergranular attack.

B. Results and Discussion

The results of long-term exposure to the three gaseous environments are shown in Table I. As noted, the gas velocity past the specimens was about 0.002 ft/sec. Each value shown represents an average for four specimens evaluated after exposure times of 240, 480, and 960 hr.

The corrosion rate of nickel-200 plate was 0.9 mil/yr for an atmosphere of 50 v/o fluorine in nitrogen, with the specimens held at about 475°C. The corrosion rates for the fluorine-hydrogen chloride environment and fluorine-oxygen environment were somewhat higher than the 50 v/o fluorine environment, but the range of values (0.9-4.1 mils/yr) indicates that only a small change in the corrosion rate occurs when a fluorine environment is alternated with either hydrogen chloride or oxygen. Metallographic examination of the specimens after exposure disclosed no evidence of intergranular penetration.

*Inert Gas Tungsten Arc process.
**The composition of these materials is given in the footnotes of Table I.

The fluorine used in these studies was purchased from the Allied Chemical Company and was passed through a heated sodium fluoride trap for the removal of hydrogen fluoride. The hydrogen chloride was purchased from the Matheson Company and used directly from the tank.

The gas environments studied were: (1) 50 v/o fluorine in nitrogen, (2) 50 v/o fluorine in nitrogen, alternated with 50 v/o hydrogen chloride in nitrogen, and (3) 50 v/o fluorine in nitrogen, alternated with 50 v/o oxygen in nitrogen. The gas mixtures were produced by metering the individual gas streams with rotometers and permitting them to mix in the inlet line before entering the furnace tube.

Nickel-plate samples, 3/4 by 2½ in., were cut from 1/16- and 1/4-in. plate. The welded specimens were made from 3/16-in. plate. The specimens were made by welding two pieces of plate, 1/2 in. by 2½ in. long, using full-penetration TIG welding* with nickel filler metal-61 or nickel filler metal-200.** The ends of the specimens were cut, and the four edges were ground with metallographic polishing paper to remove disturbed metal. The specimens were then stamped with an identifying number, degreased, and weighed. After exposure, the specimens were defilmed in an equimolar salt bath of potassium nitrate-sodium nitrate at 500°C for one-half hour. The specimens were reweighed, and the corrosion rate was calculated from the weight loss based upon the exposure time and original specimen area. Both the plate and welded specimens were sectioned, mounted in bakelite, and polished to a half-micron finish. These samples were etched, using freshly prepared and mixed solutions of 10% sodium cyanide and 10% ammonium persulfate. The samples were then examined microscopically for intergranular attack.

B. Results and Discussion

The results of long-term exposure to the three gaseous environments are shown in Table I. As noted, the gas velocity past the specimens was about 0.002 ft/sec. Each value shown represents an average for four specimens evaluated after exposure times of 240, 480, and 950 hr.

The corrosion rate of nickel-200 plate was 0.9 mil/yr for an atmosphere of 50 v/o fluorine in nitrogen, with the specimens held at about 475°C. The corrosion rates for the fluorine-hydrogen chloride environment and fluorine-oxygen environment were somewhat higher than the 50 v/o fluorine environment, but the range of values (0.9-4.1 mils/yr) indicates that only a small change in the corrosion rate occurs when a fluorine environment is alternated with either hydrogen chloride or oxygen. Metallographic examination of the specimens after exposure disclosed no evidence of intergranular penetration.

---

*Inert Gas Tungsten Arc process.
**The composition of these materials is given in the footnotes of Table I.

Table I

THE LONG-TERM CORROSION OF WELDED AND NONWELDED
NICKEL-200 PLATE IN GASEOUS ENVIRONMENTS

| | Corrosion Rate, mils/yr | | | | | | | | |
| | Nickel-200 Plate[a] | | | 61 Filler Metal Welds[b] | | | Nickel-200 Welds[c] | | |
Environment	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr
F_2 at 475[d]	0.9	0.9	0.9	1315	763	695	2.0	3.4	0.6
F_2/HCl at 450[e]	2.1	1.5	0.9	67	76	70	3.3	2.2	1.1
F_2/O_2 at 500[f]	1.9	3.8	4.1	382	673	707	5.0	4.4	2.2

[a]Nickel-200 plate, thicknesses 1/16 and 1/4 in., manufactured by the International Nickel Co., Inc., with a nominal composition in precent: Ni-99.5, C-0.06, Mn-0.25, Fe-0.15, S-0.005, Si-0.05, and Cu-0.05.

[b]These specimens were made of two pieces of nickel-200 plate, 3/16 in. thick, welded together using nickel filler metal-61 and the Inert Gas Tungsten Arc (TIG) process. The filler metal is manufactured by the International Nickel Co., Inc., and has the following nominal composition in percent: Ni-93.0, C-0.15, Mn-1.0, Fe-1.0, S-0.01, Si-0.75, Cu-0.25, Al-1.50, Ti-2.0-3.5, other 0.50. The corrosion rate was calculated by determining the weight loss after defilming, and assuming this was lost uniformly from the original weld area.

[c]These specimens were made of two pieces of nickel-200 plate, 3/16 in. thick, TIG-welded using nickel-200 filler metal. The corrosion rate was calculated by determining the weight loss of the specimen after defilming, and assuming this was lost uniformly from the total specimen area.

[d]Specimens held at 475 ± 35°C in an atmosphere of 50 v/o fluorine in nitrogen at about 1000 mm Hg absolute. Gas velocity past coupons about 0.002 ft/sec.

[e]Specimens held at 450 ± 10°C in an atmosphere of 50 v/o fluorine in nitrogen, alternated with an atmosphere of 50 v/o HCl in nitrogen every 24 hr. System pressure and gas velocity similar to those listed in item d above.

[f]Specimens held at 500 ± 25°C in an atmosphere of 50 v/o fluorine in nitrogen, alternated with an atmosphere of 50 v/o oxygen in nitrogen every 24 hr. Flow condition similar to those listed in item d above.

A comparison of the values for the corrosion rate of nickel-200 welded with weld filler metal-61, and nickel-200 welded with nickel-200 filler, shows that the welds made with nickel-200 filler have superior corrosion resistance in every instance. The high corrosion rates exhibited by the 61-filler metal welds are believed due to the presence of titanium in the filler metal. That is, the titanium present in the weld forms volatile compounds under the film of nickel fluoride that ordinarily forms a protective layer on the nickel. The pressure buildup under the film and subsequent release of pressure results in a rupture and loss of integrity of the film. X-ray analysis showed that $TiOF_2$ was the major constituent of a condensed phase in the gas stream exhausting from the test furnace in which the specimen was exposed to environment "e" of Table I.

Table 1

THE LONG-TERM CORROSION OF WELDED AND NONWELDED
NICKEL-200 PLATE IN GASEOUS ENVIRONMENTS

A comparison of the values for the corrosion rate of nickel-200 welded with weld filler metal-61, and nickel-200 welded with nickel-200 filler, shows that the welds made with nickel-200 filler have superior corrosion resistance in every instance. The high corrosion rates exhibited by the 61-filler metal welds are believed due to the presence of titanium in the filler metal. That is, the titanium present in the weld forms volatile compounds under the film of nickel fluoride that ordinarily forms a protective layer on the nickel. The pressure buildup under the film and subsequent release of pressure results in a rupture and loss of integrity of the film. X-ray analysis showed that TiOF₂ was the major constituent of a condensed phase in the gas stream exhausting from the test furnace in which the specimen was exposed to environment "e" of Table 1.

A comparison of the corrosion rates for nickel-200 plate with nickel-200 welded with nickel-200 filler metal shows that the welded specimens exhibit only slightly higher corrosion rates than the plate specimens (1-5 mils/yr compared to 1-4 mils/yr). Both welded and nonwelded specimens were examined metallographically for evidence of intergranular penetration and localized attack in areas where high-stress concentration would be expected. No such evidence was found.

III. THE CORROSION RATE OF NICKEL-200 FROM IN-PLANT TESTS

A. Materials, Apparatus, and Experimental Procedure

The corrosion rate for nickel specimens exposed to process conditions was obtained by suspending specimens in various locations within a pilot plant that was built and used to study the fluid-bed fluoride volatility processing of high-enriched uranium alloy fuels. The pilot plant is described in Ref. 2. Some specimens were also exposed in a bench-scale fluidized-bed reactor. The corrosion specimens were 1 by $2\frac{1}{2}$ in., about 25 mils thick, and drilled with a 1/4-in. hole. The procedure used to evaluate the corrosion rate from these specimens was similar to that followed in the long-term tests described in Section II.

B. Results and Discussion

The corrosion rate of nickel-200 obtained from specimens exposed to the high-enriched pilot-plant environment is shown in Table II.

Table II

THE CORROSION RATE OF NICKEL-200 PLATE FROM IN-PLANT TESTS

Test Designation	Test Identification	Test Conditions	Exposure (hr)	Corrosion Rate mils/yr	
				In Bed[a]	Out of Bed
1	Runs 1-6 Pilot-plant	Zircaloy and aluminum fuel elements without uranium reacted with (1) HCl at 440°C and (2) HF at 310°C.	59	40	35
2	Runs 1-8 Pilot-plant	Includes Runs 1-6 above, plus Runs 7 and 8 with uranium. Procedure for Runs 7 and 8 included (1) HCl at 440°C, (2) HF at 310°C, and (3) F_2 at 250-500°C.	92	37	27
3	Run 10-attrition Run-pilot-plant	Attrition run performed without fuel charge (1) HCl at 380°C, (2) HF at 355°C, and (3) F_2 at 390°C. Run 10 conditions below.	2[f]	35	-
4	Run 10	Aluminum-uranium alloy charge (1) HCl at 370°C, (2) HF at 360°C, and (3) F_2 at 250-500°C.	28	-	12
5	Runs 13, 14 and 15 Pilot-plant	Zircaloy-2 uranium alloy charge (1) HCl at 360-390°C, (2) HF at 360°C, and (3) F_2 at 250-520°C.	76	40	31

[a]The bed consisted of 28 to 100 mesh, high-fired alumina, fluidized at a velocity of approximately 0.6 ft/sec.

A comparison of the corrosion rates for nickel-200 plate with nickel-200 welded with nickel-200 filler metal shows that the welded speci-mens exhibit only slightly higher corrosion rates than the plate specimens (1-6 mils/yr compared to 1-4 mils/yr). Both welded and nonwelded speci-mens were examined metallographically for evidence of intergranular pen-etration and localized attack in areas where high-stress concentration would be expected. No such evidence was found.

III. THE CORROSION RATE OF NICKEL-200 FROM IN-PLANT TESTS

A. Materials, Apparatus, and Experimental Procedure

The corrosion rate for nickel specimens exposed to process condi-tions was obtained by suspending specimens in various locations within a pilot plant that was built and used to study the fluid-bed fluorine volatility processing of high-enriched uranium alloy fuels. The pilot plant is de-scribed in Ref. 4. Some specimens were also exposed in a bench-scale fluidized-bed reactor. The corrosion specimens were 1 by 2 in., about 25 mils thick, and drilled with a 1/4-in. hole. The procedure used to evaluate the corrosion rate from these specimens was similar to that fol-lowed in the long-term tests described in Section II.

B. Results and Discussion

The corrosion rate of nickel-200 obtained from specimens exposed to the high-enriched pilot-plant environment is shown in Table II.

As is shown, the corrosion rate for in-plant exposed specimens ranged from 12-40 mils/yr, with the higher values obtained for the specimens in contact with the fluidized alumina bed. Visual observation of the specimens in contact with the fluidized bed after removal from the reactor showed the specimens to be polished to a satin finish. The hole drilled to support the specimens was found to be slightly enlarged. This was determined to be due to the movement of the coupon against its supporting peg by the action of the fluid bed. Since this erosion effect is small and difficult to access, the corrosion-rate calculations were made including the erosion loss along with corrosion loss. The values reported for the in-bed specimens are conservative, i.e., higher than will be experienced by a fixed surface in plant equipment. The specimens were defilmed and their corrosion rates calculated in the manner previously described. Representative samples were polished, etched, and examined microscopically for evidence of intergranular corrosion. In general, no such evidence was found. Several specimens exhibited a few areas where apparent intergranular attack to a depth of 1-2 mils had occurred. The maximum penetration found for all the specimens examined was 4 mils.

IV. THE EFFECT OF THERMAL CYCLING UPON THE CORROSION RATE OF NICKEL-200 IN A "STATIC" FLUORINE ENVIRONMENT

In this test, a furnace tube containing corrosion specimens was maintained continuously at 550 ± 10°C and was fed a mixture of 50 v/o fluorine in nitrogen at 5 ± 1 psig for 8 hr each day. For the remainder of each day, a purge of nitrogen only was maintained. A second reactor in series with the first received the same reactants for the same times, but the temperature was maintained at 550 ± 10°C only for the 8 hr of fluorine exposure, following which it was cooled to room temperature and reheated to 550°C before the next cycle.

Two types of specimens were used: 3/16-in. nickel-200 plate, and 3/16-in. nickel-200 plate with a machined "V" notch filled with nickel-200 weld metal. The weld metal was laid down by the TIG welding procedures, and the beads were ground flush. Triplicates of the specimens were included in each reactor. Both reactors received 10 cycles (80 hr total exposure to fluorine). After exposure, the specimens were defilmed in an equimolar bath of KNO_3-$NaNO_3$ at 500°C for 15 min and weighed. The results of these tests are shown in Table III. The effect of thermal cycling under these conditions is negligible.

As is shown, the corrosion rate for in-plant exposed specimens ranged from 12-40 mils/yr) with the higher values obtained for the specimens in contact with the fluidized alumina bed. Visual observation of the specimens in contact with the fluidized bed after removal from the reactor showed the specimens to be polished to a satin finish. The hole drilled to support the specimens was found to be slightly enlarged. This was determined to be due to the movement of the coupon against its supporting peg by the action of the fluid bed. Since this erosion effect is small and difficult to assess, the corrosion-rate calculations were made including the erosion loss along with corrosion loss. The values reported for the in-bed specimens are conservative, i.e., higher than will be experienced by a fixed surface in plant equipment. The specimens were declined and their corrosion rates calculated in the manner previously described. Representative samples were polished, etched, and examined microscopically for evidence of intergranular corrosion. In general, no such evidence was found. Several specimens exhibited a few areas where apparent intergranular attack to a depth of 1-2 mils had occurred. The maximum penetration found for all the specimens examined was 4 mils.

IV. THE EFFECT OF THERMAL CYCLING UPON THE CORROSION RATE OF NICKEL-200 IN A "STATIC" FLUORINE ENVIRONMENT

In this test, a furnace tube containing corrosion specimens was maintained continuously at $550 \pm 10^{\circ}$C and was fed a mixture of 50 v/o fluorine in nitrogen at 5 ± 1 psig for 8 hr each day. For the remainder of each day, a purge of nitrogen only was maintained. A second reactor in series with the first received the same reactants for the same times, but the temperature was maintained at $550 \pm 10^{\circ}$C only for the 8 hr of fluorine exposure, following which it was cooled to room temperature and reheated to 550°C before the next cycle.

Two types of specimens were used: 3/16-in. nickel-200 plate, and 3/16-in. nickel-200 plate with a machined "V" notch filled with nickel-200 weld metal. The weld metal was laid down by the TIG welding procedures, and the beads were ground flush. Triplicates of the specimens were included in each reactor. Both reactors received 10 cycles (80 hr total exposure to fluorine). After exposure, the specimens were declined in an equimolar bath of RNO_3, $NaNO_3$ at 500°C for 15 min and weighed. The results of these tests are shown in Table III. The effect of thermal cycling under these conditions is negligible.

Table III

THE EFFECT OF THERMAL CYCLING UPON THE CORROSION RATE
OF WELDED AND NONWELDED NICKEL-200 PLATE

Conditions:

Temperature: 550°C
Reagent Gas: 50 v/o F_2 in N_2
Flow Velocity: About 0.002 ft/sec

	Corrosion Rate, mils/yr	
	Constant Temperature	Thermal Cycled
Nickel Plate	2.6	3.9
Welded Nickel	6.2	4.6

V. THE EFFECT OF AIR EXPOSURE UPON THE CORROSION RATE OF NICKEL-200 EXPOSED TO HCl AND FLUORINE

A test was made that examined the effect of exposing nickel-200 corrosion coupons to the air after they had been exposed to HCl and F_2 at process temperatures. The conditions and results of this test are shown in Table IV.

Table IV

THE EFFECT OF AIR EXPOSURE UPON THE CORROSION RATE
OF NICKEL-200 EXPOSED TO HCl AND FLUORINE

Specimens were exposed in two furnace tubes each of which were subjected to three cycles of reagents and temperatures as shown below. Between cycles, each furnace tube was allowed to cool to room temperature overnight under nitrogen. While at room temperature, one of the tubes was evacuated and subjected to the flow of room air for one hour, while the other was maintained under nitrogen.

Type of Specimen	Air-exposed		N_2 Blanket	
	mils/cycle[a]	mils/yr[b]	mils/cycle[a]	mils/yr[b]
Nickel Plate	0.011	10	0.010	8
Welded Plate	0.015	13	0.010	8

[a]1 cycle = 6 hr 50% HCl/H_2 at 375°C
3 hr 50% F_2/N_2 at 375-500°C
Flow Rate: About 0.002 ft/sec.

[b]Based upon one-calendar-year exposure (8750 hr).

Table III

THE EFFECT OF THERMAL CYCLING UPON THE CORROSION RATE OF WELDED AND NONWELDED NICKEL-200 PLATE

Conditions:

Temperature: 550°C
Reagent Gas: 80% F_2 in N_2
Flow Velocity: About 0.002 ft/sec

	Corrosion Rate, mils/yr	
	Constant Temperature	Thermal Cycled
Nickel Plate	2.8	7.5
Welded Nickel	4.2	5.8

V. THE EFFECT OF AIR EXPOSURE UPON THE CORROSION RATE OF NICKEL-200 EXPOSED TO HCl AND FLUORINE

A test was made that examined the effect of exposing nickel-200 corrosion coupons to the air after they had been exposed to HCl and F_2, at process temperatures. The conditions and results of this test are shown in Table IV.

Table IV

THE EFFECT OF AIR EXPOSURE UPON THE CORROSION RATE OF NICKEL-200 EXPOSED TO HCl AND FLUORINE

Specimens were exposed in two furnace tubes, each of which were subjected to three cycles of reagents and temperatures as shown below. Between cycles, each furnace tube was allowed to cool to room temperature overnight under nitrogen. While at room temperature, one of the tubes was evacuated and subjected to the flow of room air for one hour, while the other was maintained under nitrogen.

	N_2 Blanked		Air-exposed		
Type of Specimen	mils/cycle[a]	mils/yr[b]	mils/cycle[a]	mils/yr[b]	cycles
Nickel Plate	0.011	16	0.010	15	3
Welded Plate	0.013	19	0.016	23	3

[a] 1 cycle = 4 hr 50% HCl/N_2 at 375°C
    + 4 hr 50% F_2/N_2 at 375-550°C

Flow Rate: About 0.002 ft/sec

[b] Based upon one-calendar-year-exposure rate (4380 hr).

As is shown by the results in Table IV, the specimens that were air-exposed exhibited slightly higher corrosion rates than those kept under nitrogen. For all practical purposes, this difference is not considered significant.

VI. THE EFFECT OF A FLUIDIZED BED OF ALUMINA UPON THE CORROSION RATE OF NICKEL-200 PLATE

Two runs have been conducted in the Senior Cave bench-scale equipment in which the effect of a fluidized bed of alumina upon the corrosion rate of nickel-200 plate was examined. The specimens were fastened so as to prevent their movement and hence eliminate erosive effects. The results and conditions of these runs are given in Table V.

Table V

THE EFFECT OF A FLUIDIZED ALUMINA BED UPON THE CORROSION RATE OF NICKEL-200 PLATE

Run 1 - Prefluorination at 25-450°C for $2\frac{3}{4}$ hr; HCl at 370°C for 8 hr. Fluorination at 250-500°C for 4 hr. Duplicate specimens exposed. No alumina bed in the reaction zone of the reactor. Alumina bed present in the fixed-bed filter.

Run 2 - Conditions similar to Run 1, except an alumina bed was added to the reaction zone of the reactor. Gas velocities were such as to maintain the alumina fluidized, except for the latter part of the fluorination step.

Specimen Locations	Corrosion Rate, mils/yr	
	Run 1, No Bed	Run 2, Alumina Bed[a]
Reaction zone of reactor	11	23
Disengaging section	18	16
Fixed-bed filter	12	9

[a]Alcoa T-61 Alumina, 28-100 mesh.

As shown, the presence of an alumina bed when fluidized increases the corrosion rate significantly (11 mils/yr without bed, 23 mils/yr with bed). The presence of the alumina under nonfluidized conditions does not appear to affect the corrosion rate as seen by comparing the rate obtained (Run 1) in the fixed-bed filter with that in the reaction zone in the reactor (12 mils/yr compared to 11 mils/yr).

As is shown by the results in Table IV, the specimens that were air-exposed exhibited slightly higher corrosion rates than those kept under nitrogen. For all practical purposes, this difference is not considered significant.

VI. THE EFFECT OF A FLUIDIZED BED OF ALUMINA UPON THE CORROSION RATE OF NICKEL-200 PLATE

Two runs have been conducted in the Senior Cave bench-scale equipment in which the effect of a fluidized bed of alumina upon the corrosion rate of nickel-200 plate was examined. The specimens were fastened so as to prevent their movement and hence eliminate erosive effects. The results and conditions of these runs are given in Table V.

Table V

THE EFFECT OF A FLUIDIZED ALUMINA BED
UPON THE CORROSION RATE OF NICKEL-200 PLATE

Run 1 – Prefluorination at 25–450°C for 24 hr; HCl at 370°C for 8 hr. Fluorination at 250–500°C for 4 hr. Duplicate specimens exposed. No alumina bed in the reaction zone of the reactor. Alumina bed present in the fixed-bed filter.

Run 2 – Conditions similar to Run 1, except an alumina bed was added to the reaction zone of the reactor. Gas velocities were such as to maintain the alumina fluidized, except for the latter part of the fluorination step.

| | Corrosion Rate, mils/yr | |
Specimen Locations	Run 1, No Bed	Run 2, Alumina Bed[a]
Reaction zone of reactor	11	23
Disengaging section	18	16
Fixed-bed filter	12	9

[a] Alcoa T-61 Alumina, 28–100 mesh.

As shown, the presence of an alumina bed when fluidized increases the corrosion rate significantly (11 mils/yr without bed, 23 mils/yr with bed). The presence of the alumina, under nonfluidized conditions does not appear to affect the corrosion rate as seen by comparing the rate obtained (Run 1) in the fixed-bed filter with that in the reaction zone in the reactor (12 mils/yr compared to 11 mils/yr).

VII. A COMPARISON OF THE CORROSION TEST RESULTS WITH REACTION RATE DATA FOR NICKEL IN FLUORINE

In an attempt to understand the corrosion process and to evaluate the relative importance of particular parameters under study in the laboratory tests, the results of the laboratory tests were compared with the results of the in-plant tests and with chemical reaction kinetic data.

The laboratory test data (Section II) obtained for fluorine, fluorine alternated with HCl, and fluorine alternated with oxygen, are compared (Figure 1) with corrosion values calculated from a kinetic study of the reaction between nickel and fluorine. The laboratory values shown are the average values obtained from exposure periods of 240, 480, and 960 hr. The comparison shows that the rates obtained in the laboratory tests are in close agreement with the values found for pure fluorine in the kinetic study. It is important to note that the comparison is made for specimens that have been exposed to the reactants for a long period of time under conditions of "static" reagent supply that permit protective films to form. As can be seen from Figure 11, p. 18 of Ref. 1, the rate of change of the reaction rate between nickel and fluorine with time after an exposure of 33 hr becomes small, and the comparison made in Figure 1 (exposures of 240 hr and higher) is valid. Under these conditions, the conclusion may be made that alternating a fluorine environment with HCl or with oxygen does not significantly increase the corrosion rate.

Figure 1

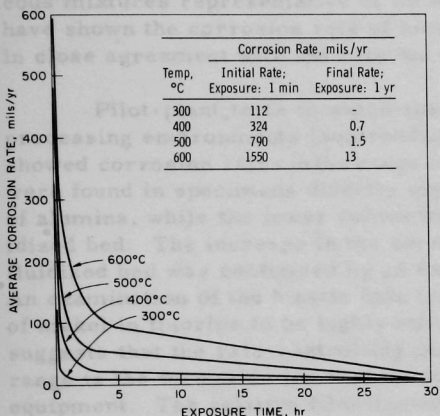### THE LONG-TERM CORROSION OF NICKEL-200 IN STATIC GASEOUS ENVIRONMENTS
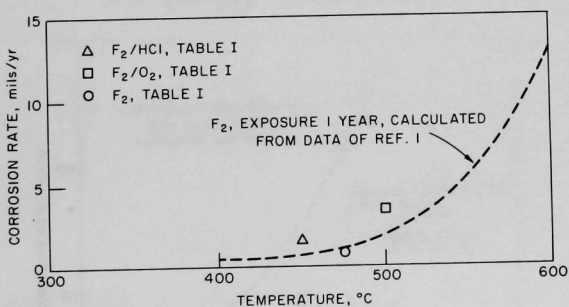
The protective nature of the nickel fluoride film is illustrated in Figure 2. As is shown, the corrosion rate is very rapid initially and decreases markedly as the film of nickel fluoride increases in thickness; therefore, the corrosion rate will be highly dependent upon the thickness of the film that exists at any particular time. In process equipment, where fairly high gas velocities exist and/or there is attrition due to fluidized

VII. A COMPARISON OF THE CORROSION TEST RESULTS WITH
REACTION RATE DATA FOR NICKEL IN FLUORINE

In an attempt to understand the corrosion process and to evaluate the relative importance of particular parameters under study in the laboratory tests, the results of the laboratory tests were compared with the results of the in-pit tests and with chemical reaction kinetic data.

The laboratory test data (Section II) obtained for fluorine, fluorine alternated with HCl, and fluorine alternated with oxygen, are compared (Figure 1) with corrosion values calculated from a kinetic study of the reaction between nickel and fluorine. The laboratory values shown are the average values obtained from exposure periods of 250, 550, and 960 hr. The comparison shows that the values obtained in the laboratory tests are in close agreement with the values found for pure fluorine in the kinetic study. It is important to note that the comparison is made for specimens that have been exposed to the reactants for a long period of time under conditions of "static" reagent supply (i.e. partial pressure-time to form). As can be seen from Figure 11, (p. 18 of Ref.), the rate of change of the reaction rate between nickel and fluorine with time after an exposure of 15 hr becomes small, and the comparison made in Figure 1 (exposures of 250 hr and higher) is valid. Under those conditions, the conclusion may be made that alternating a fluorine environment with HCl or with oxygen does not significantly increase the corrosion rate.

Figure 1

THE LONG-TERM CORROSION OF NICKEL-200
IN STATIC GASEOUS ENVIRONMENTS

The protective nature of the nickel fluoride film indicated in Figure 1. As is shown, the corrosion rate is very rapid initially and decreases markedly as the nickel fluoride increases in thickness; therefore, the corrosion rate will be highly dependent upon the thickness of the film that exists at any particular time. In process equipment, where fairly high gas velocities exist and/or there is attrition due to fluidized

Figure 2

CORROSION OF NICKEL IN FLUORINE AS A
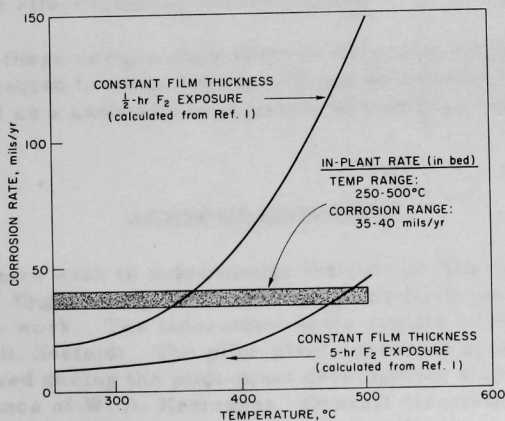FUNCTION OF TEMPERATURE AND TIME

Based upon data from Ref. 1

Temp, °C	Corrosion Rate, mils/yr	
	Initial Rate; Exposure: 1 min	Final Rate; Exposure: 1 yr
300	112	-
400	324	0.7
500	790	1.5
600	1550	13

bed of alumina, films formed under quiescent conditions will be removed to some extent. Results obtained in both the laboratory studies and from the pilot-plant studies show that the corrosion rate is increased by the action of a fluidized bed of alumina, indicating some film removal. To estimate the extent of this film removal, the corrosion rate of specimens exposed to the action of a fluidized bed was plotted and compared with the corrosion rate of nickel in fluorine having constant film thicknesses. The effect of the presence of other gases (HCl, O₂) has been shown to be small in the long-term laboratory tests and can be neglected for purposes of this comparison. As is shown by this plot (Figure 3), the in-plant specimens exposed to a fluidized bed behave as though they are protected by a thin film equivalent to what would be produced by an exposure to fluorine under static conditions for 5 hr or less.

Figure 3

COMPARISON OF IN-PLANT CORROSION RATES
WITH KINETIC RATE DATA FROM REF. 1

bed of alumina, films formed under quiescent conditions will be removed to some extent. Results obtained in both the laboratory studies and from the pilot-plant studies show that the corrosion rate is increased by the action of a fluidized bed of alumina, indicating some film removal. To estimate the extent of this film removal, the corrosion rate of speci- mens exposed to the action of a fluidized bed was plotted and com- pared with the corrosion rate of nickel in fluorine having constant film thicknesses. The effect of the presence of other gases (HCl, O_2) has been shown to be small in the long-term laboratory tests and can be neglected for purposes of this comparison. As is shown by this plot (Figure 3), the in-plant speci- mens exposed to a fluidized bed

behave as though they are protected by a thin film equivalent to what would be produced by an exposure to fluorine under static conditions for 5 hr or less.

Figure 2

CORROSION OF NICKEL IN FLUORIDE AS A FUNCTION OF TEMPERATURE AND TIME

Based upon data from Ref. 1

Figure 3

COMPARISON OF IN-PLANT CORROSION RATE WITH KINETIC RATE DATA FROM REF. 1

VIII. SUMMARY

Corrosion data from both laboratory tests and in-plant exposure tests have been obtained. Long-term exposures in essentially static gaseous mixtures representative of fluid-bed fluoride volatility environments have shown the corrosion rate of nickel-200 to be low (1-4 mils/yr) and in close agreement with the rate for nickel in fluorine alone.

Pilot-plant tests in which specimens were exposed to the actual processing environments (nonirradiated uranium alloys were processed) showed corrosion rates in the range of 12-40 mils/yr. The higher values were found in specimens directly exposed to the action of a fluidized bed of alumina, while the lower values were found in areas outside the fluidized bed. The increase in the corrosion rate due to the action of the fluidized bed was confirmed by an experiment in bench-scale apparatus. An examination of the kinetic data from Ref. 1 shows the corrosion rate of nickel in fluorine to be highly influenced by the film thickness and suggests that the rate-controlling parameter for a particular temperature range is the formation (or destruction) of protective films within the equipment. The relative film thickness was estimated by comparing in-plant data obtained from specimens in contact with the fluidized bed with kinetic data. This comparison shows that complete film removal is not obtained and the specimens behave as though they are protected by a thin film equivalent to what would be produced by a static exposure to fluorine for a few hours.

In addition, several other parameters that were assumed to have a possible effect upon the protective film formed within the equipment were examined in laboratory tests. Neither thermal cycling nor air exposure had a significant effect upon the corrosion rate.

Finally, these results show that the corrosion rates in plant equipment can be expected to range between 12 and 40 mils/yr and that nickel can be regarded as a satisfactory material of construction for many plant applications.

ACKNOWLEDGMENTS

REFERENCES

1. Jarry, R. L., Gunther, W. H., and Fischer, J., The Mechanism and Kinetics of the Reactions between Nickel and Fluorine, ANL-6684 (August 1963).

2. Holmes, J. T., Stethers, H. L., and Barghusen, J. J., Engineering Development of Fluid-bed Fluoride Volatility Processes. Part 8. Pilot Plant Development of a Process for Uranium Alloy Fuels, ANL-6973 (to be published).

REFERENCES

1. Jerry, R. L., Gunther, W. H., and Fischer, J., The Mechanism and Kinetics of the Reactions between Nickel and Fluorine, ANL-6684 (August 1963).

2. Holmes, J. T., Stethers, H. L., and Bergeman, J. J., Engineering Development of Fluid-bed Fluoride Volatility Processes. Part 8. Pilot Plant Development of a Process for Uranium Alloy Fuels, ANL-6973 (to be published).